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THE PREPARATION OF PURE OSMIUM

THE ATOMIC WEIGHT OF OSMIUM

By

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Dissertation

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THE PREPARATION OF PURE OSMIUM

THE ATOMIC WEIGHT OF OSMIUM

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THE PREPARATION OF PURE OSMIUM
THE ATOMIC WEIGHT OF OSMIUM

General Introduction

In undertaking the problem of the determination of the atomic weight of osmium it became apparent that the literature contained no satisfactory method for the preparation of the pure metal.

Even in the cases where the best work had been done upon the atomic weight, the osmium used for the preparation of the samples for analysis was taken "on faith" to be of the highest purity. No critical tests were made of its purity, nor was the method of preparation divulged, the latter being a "secret".

It was necessary, therefore, to develop a procedure by which pure osmium could be prepared.

The first part of this paper deals with the question of the preparation of osmium of highest possible purity. The second part is concerned with the determination of the atomic weight.

PREPARATION OF PURE OSMIUM

1. Introduction

A procedure was sought which would satisfy two requirements. First that it would produce osmium of the highest possible purity and second that it would lend itself to the convenient preparation of large amounts of pure metal.

The methods given in the literature were not suitable for one reason or another.

The compound of osmium which enters into any process of purification is the volatile tetroxide. The ease with which osmium forms this compound makes its separation from the other platinum metals a matter of simplicity. On the other hand, this same property renders the subsequent handling of this element a matter of considerable difficulty. Unlike the other platinum metal solutions, osmium solutions are, in general, unstable and there is an every constant loss of this metal as the volatile tetroxide.

2. Methods of Preparation of Metallic Osmium Given in the Literature.

Vauquelin[1] precipitated metallic osmium from an acidified

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[1] Annales Chim. 89, 150 (1814)

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alkaline osmate solution by means of zinc.

Berzelius[1] agitated the acidified osmate solution with

[1] Ann. de Chim. et Phys., 2e Serie, 40, 258 (1829)

mercury which displaced the osmium and formed an amalgam with it. The mercury was removed by heating in a current of hydrogen. This method of extraction by amalgamation is practically the same as that used by Tennant (1804) in isolating the metal for the first time.

Doebereiner[2] made use of the alkali formate reduction.

[2] Liebig's Annalen, 14, 17 (1835)

Berzelius obtained metallic osmium in the dry way by passing the vapors of OsO_4 mixed with hydrogen through a glass tube which was heated to redness for a portion of its length. The metal deposited on the walls of the tube.

Deville and Debray[3] obtained the metal by passing OsO_4

[3] Compt. rend. 82, 1076 (1876)

vapors and carbon monoxide, or carbon monoxide and carbon dioxide, through a porcelain tube heated to redness. They likewise obtained the metal by passing OsO_4 vapors and nitrogen through a porcelain tube heated to redness, in which previously a deposit of carbon had been produced from benzene.

Berzelius[4] warmed a solution of OsO_4 in concentrated

[4] Ann. de Chim. et Phys. 42, 191 (1829)

NH_4OH at 40° to 50°C for some hours. The liquid, yellow at first, darkened on the evolution of nitrogen, and finally deposited a dark brown powder, osmium diammine hydroxide, insoluble in water but soluble in excess NH_4OH. The reaction was complete at the end of a few days and complete precipitation of the compound was obtained by evaporation.

$$3\ OsO_4 + 10\ NH_3 \rightarrow 3\ OsO(NH_3)_2(OH)_2 + 2\ N_2 + 3\ H_2O$$

The osmium diammine hydroxide was converted to osmium diammine chloride by means of HCl. The chloride was evaporated to dryness and heated in a retort until HCl ceased to be evolved. Metallic osmium remained.

Woehler[1] added an excess of NH_4Cl to a solution of OsO_4

[1] Ann. de Chim. et Phys. 2e Série, 54, 318 (1833)

in KOH, evaporated to dryness and ignited to dull redness in the absence of air. Osmium metal remained after extraction of soluble salts with water.

Fremy[2] treated the solution of OsO_4 in KOH with a little

[2] Ann. de Chim. et Phys. 3e Série, 44, 391 (1855)
3e Série, 12, 521 (1844)

alcohol which caused the reduction of the oxide and precipitated rose colored crystalline potassium osmate, K_2OsO_4, insoluble in alcoholic water. This compound treated with a concentrated solution of NH_4Cl yielded osmyl tetra-ammine chloride, $OsO_2(NH_3)_4Cl_2$.

$$K_2OsO_4 + 4\ NH_4Cl \rightarrow OsO_2(NH_3)_4Cl_2 + 2\ KCl + 2\ H_2O$$

Reduction of this compound in hydrogen gave metallic osmium.

W. von Schneider[1] avoided the passage to the state of

[1] Liebig's Annalen Supplbd. V, 267 (1867)

the alkaline osmate. He attacked the osmiridium mixed with NaCl directly with moist chlorine at dull redness, a method used by Wcehler[2], and caught the OsO_4 and HCl evolved in

[2] Pogg. Annalen 31, 161 (1834)

alcohol. An excess of NH_4OH gave osmyl-tetra-ammine chloride which was recrystallized from boiling water and reduced in the absence of air.

Deville and Debray[3] distilled OsO_4 into dilute NH_4OH

[3] Ann. des Mines, 5e Série, 16, 11 (1859)
C.f. Encyclopédie Chimique (Fremy) Vol. 30 (Part 1) pp. 6-9)

and precipitated the metal as a sulphide. The carefully dried sulphide was reduced to metal by heating in a covered carbon crucible for four to five hours.

3. The Reaction of Osmium Tetroxide

(a) In the presence of dilute hydrochloric acid and alcohol --

The crux of the procedure which was developed for the purification of osmium was the ability to pass from osmium tetroxide to the quadrivalent osmium halide.

Moraht and Wischin[1] described an experiment in which

[1] Z. Anorg. Chem. 3, 167 (1893)

they heated on a water-bath in a reflux apparatus the black solid osmic acid, H_2OsO_4, with concentrated hydrochloric acid and alcohol. The deeply colored olive green liquid obtained could not be concentrated on the water-bath without undergoing decomposition and the deposition of a black precipitate.

On evaporation in the cold over concentrated sulphuric acid and also fused potassium hydroxide, they obtained, after a long time, the complete removal of excess water and hydrochloric acid and the deposition of crystals having the appearance of hexagonal pyramids. These dry crystals had the color of the red oxide of lead, but on contact with moist air they became deep olive green. They were soluble in alcohol, giving the green solution, from which they could be recrystallized.

Analysis lead to the attribution of the formula

$$Os_2Cl_7 \cdot 7\ H_2O.$$

Potassium chloride precipitated from the alcoholic solution one-half the osmium present as K_2OsCl_6. The osmium remaining was the deep olive green hydrated osmium trichloride.

This experiment served as a basis for speculation. By substituting osmium tetroxide for osmic acid, and 6 N hydrochloric for concentrated acid the reaction took place with

greater ease, required less time and did not form osmium trichloride. The reaction was complete in three hours. The solution had no odor whatsoever of osmium tetroxide and could be evaporated to a syrup on the steam-bath without decomposition.

NH_4Cl precipitated the characteristic brick red $(NH_4)_2OsCl_6$ from diluted golden yellow H_2OsCl_6 solution.

(b) In the presence of dilute hydrobromic acid --

As it was necessary to prepare ammonium bromosmate for atomic weight analyses this same reaction was used to make bromosmic acid.

The reaction between osmium tetroxide and 30 per cent hydrobromic acid proceeded with far greater ease than was the case with hyarochloric acid. The reaction commenced in the cold and did not require the addition of alcohol. Heating at incipient boiling for one-half an hour was sufficient to complete the reaction.

The deep red solution of bromosmic acid suffered no decomposition on evaporation to syrupy consistency, nor was the odor of OsO_4 perceptible.

From the diluted solution NH_4Br precipitated $(NH_4)_2OsBr_6$, a black compound with a faint tinge of brown.

4. The Crude Material

The crude material consisted of 2253 g of residues[1], a

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[1] Loaned to Bureau of Standards by Nitrate Division of Ordnance Department. Afterwards permanently transferred to Dept. of Commerce, Bureau of Standards, by the War Dept.

portion of which was obtained in the refining of a 21 000-ounce lot of crude platinum[2] by the U. S. Assay Office in New York. The residues consisted principally of platinum, iridium and osmium together with considerable quantities of iron and tin and lesser amounts of other base metals. A sample has been reserved for analysis when opportunity permits.

[2] Brought to the U. S. from the Ural Mountains in 1917 by F. W. Draper, Mineral Industry, Vol. 26, pp. 550-555 (1917)

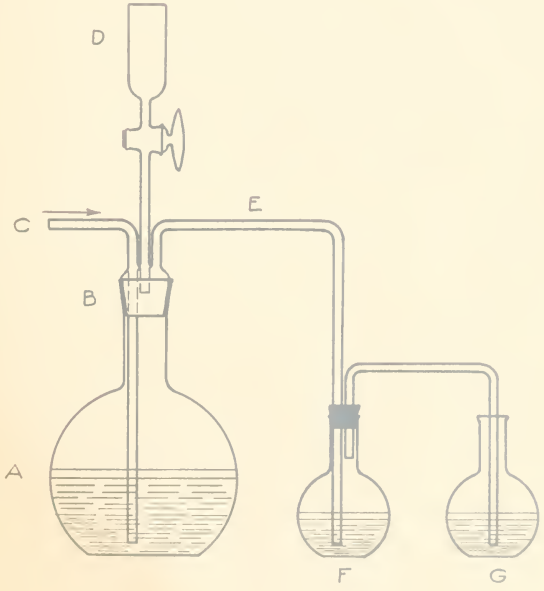
Unfortunately two sets of residues had been united to form the 8253-g lot. One set was a portion of the aqua regia insoluble from the original 21 000 ounce mass of crude platinum. The other was a portion of the metals recovered from the filtrates of NH_4Cl precipitations of platinum.

In the residues received there was supposed to have been about 310 g of osmium but actually there was about 100 g.

5. The Concentration of Osmium from the Crude Material

The first step in the concentration of the osmium was to separate the residues again into an aqua regia soluble portion and an insoluble portion. This was done with concentrated aqua regia which gave 1033 g of insoluble material.

Apparatus For The Distillation of Osmium Tetroxide From The Acidified Solution of The Alkaline-Nitrate Fusion



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The greater portion of the insoluble was fused directly with commercial NaOH and $NaNO_3$ in the proportions, osmiridium (100 g), $NaNO_3$ (300 g), NaOH (300 g). The remainder of the insoluble was subjected to a roasting at 850° - 900°C in a current of oxygen before making the alkaline-nitrate fusion.

Silver dishes were firstemployed for the fusion but later one-liter gold dishes were used. The molten bath "crept" considerably in the case of the silver, but scarcely at all when gold was used. Quartz plates were used to cover the dishes during fusion.

The heating was done by an electric muffle furnace at about 900°C for 2-1/2 to 3 hours.

The water soluble portions of the fusions were placed in a distillation apparatus (see sketch). Concentrated HNO_3 was added slowly through the funnel. When enough HNO_3 had been added to render the solution distinctly acid, the temperature was gradually raised to the boiling point.

A current of air passing through the apparatus swept the volatile OsO_4 into the receiving flasks where it was absorbed by 10 per cent NaOH containing a little alcohol. The alcohol reduced the OsO_4 to OsO_3 forming Na_2OsO_4.

The OsO_4 obtained from the direct oxidation of the osmiridium was absorbed in the same manner.

The water insoluble portions of the alkaline-nitrate fusion were repeatedly treated with the molten alkali bath until complete solution was effected.

The Na_2OsO_4 solutions were subjected to a second distillation. During this distillation it was observed that it was not possible to remove all of the osmium. The solution in the flask became deep red. Further addition of HNO_3 failed to liberate anything but a trace of OsO_4. Nor would aqua regia cause OsO_4 to distil out. Rendering the solution alkaline and again acid was of no avail. The exact nature of the stable compound formed was not investigated for lack of time.

According to Wintrebert[1], HCl acts on K_2OsO_4 to form

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1 Ann. Chim. Phys. 28, 15 (1903)

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osmyl-oxy compounds, oxmyl compounds and even chlorosmates.

K_2OsO_4	$\rightarrow$ $K_2OsO_2 \cdot OCl_2$	$\rightarrow$ $K_2OsO_2 \cdot Cl_4$	$\rightarrow$ K_2OsCl_6
potassium osmate	potassium osmyl-oxy chloride	potassium osmyl chloride	potassium chlorosmate

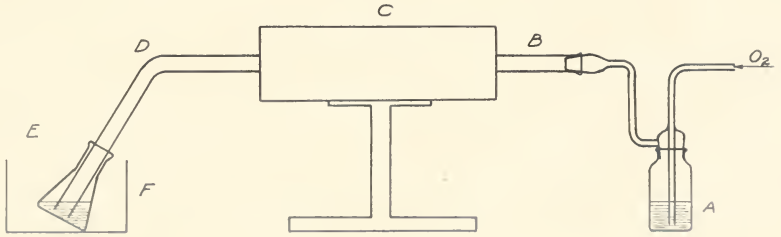
Perhaps the stable compound here may be such a thing as $Na_2 \cdot OsO_2 \cdot (NO_3)_4$, sodium osmyl nitrate.

A current of chlorine passing through the alkaline solution of this red compound at temperatures near 100°C removed the osmium completely, as tetroxide.

If no alcohol had been added to the OsO_4 solution in NaOH, all of the osmium could be distilled out from the solution, acid with HNO_3.

The alkaline osmate solutions from the second distillation were electrolyzed, using platinum foil electrodes 1-1/2 cm x 3-1/2 cm and a current up to 2 amperes.

Apparatus For The Preparation of Osmium Textroxide



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OsO_2 separated at the cathode[1] as a black loosely adherent deposit. No odor of OsO_4 was observed at any time during these electrolyses.

[1] Moraht and Wischin, Z. anor. Chem. 3, 153 (1893)

It was not possible to wash the OsO_2 free of alkali. The dried OsO_2 was reduced to metal in hydrogen.

Spectroscopic examination of this material showed it to be free from the other platinum metals, but did contain alkali and impurities from the NaOH used, for instance, iron.

6. The preparation of Pure Osmium

The osmium obtained from the electrolysis of the alkaline osmate solutions served as a starting point in the preparation of the pure metal.

(a) Preparation of Osmium Tetroxide

The apparatus for the preparation of osmium tetroxide consisted of a Drechsel bottle (A) contining conc. H_2SO_4, a tube (B) whose bent arm (D) extended into an Erlenmeyer flask (E). (E) contained 6 N HCl and was jacketed by an ice bath (F). (C) was a Hoskins split tube furnace. See sketch.

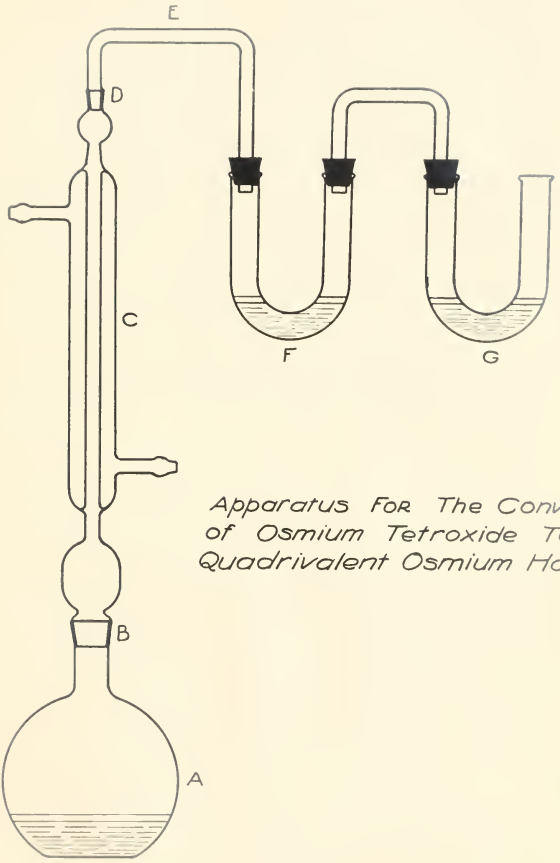
An electric furnace (Hoskins Type 70), split such that its upper half could be raised at will, was used for heating the combustion tube.

The Erlenmeyer flask was surrounded by an ice pack.

The Drechsel wash bottle containing conc. H_2SO_4 preceding the combustion tube served as an indicator for the flow of oxygen.

The osmium metal in porcelain boats was placed in the horizontal arm of the combustion tube. Vapors of OsO_4 soon appeared in the cool arm of the tube. A visible reaction took place long before the furnace reached dull redness. It was accompanied by a rapid absorption of oxygen and a passing glow over the surface of the metal in the direction of the oxygen current. Care was taken to supply oxygen at this stage in quantity sufficient to keep the liquid in the lower arm of the combustion tube at constant level. The material in the boat became black and probably was the dioxide. When the glow disappeared, the material in the boats absorbed oxygen slowly and quietly until all the osmium was converted to OsO_4, in case one were working on pure osmium. The temperature at the end was that of dull redness of the heating coils.

The OsO_4 condensed in the cool arm of the combustion tube in the form of white feathery crystals and en masse as the liquid OsO_4 froze, in which case it had a faint yellowish green color. A little alcohol was always added to the HCl in the Erlenmeyer flask. Only a faint odor of OsO_4 emanated from the flask. Any amount of OsO_4 could be prepared in this manner by merely recharging the porcelain boats.



Apparatus For The Conversion of Osmium Tetroxide To Quadrivalent Osmium Halide.

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WASHINGTON, D. C.
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When sufficient OsO_4 had been made, the lower arm of the combustion tube was gently warmed as far as the neck of the Erlenmeyer flask with a Bunsen flame, to cause the OsO_4 to melt and run into the Erlenmeyer. A stream of hot .6 N HCl from a wash bottle warmed the end of the tube enough to cause all the OsO_4 to drop into the flask. The mass was then quickly transferred to the reduction flask where it could be allowed to remain.

It may be said here that although one is handling concentrated osmium tetroxide there is no danger involved. Only during the process of transferring the compound from the tube to the reduction flask does one come in contact with the vapor, and then only for an instant.

(b) Conversion of OsO_4 to H_2OsCl_6

The apparatus used for the conversion of osmium tetroxide to the quadrivalent halide consisted of a two-liter pyrex flask (A) fitted by a ground glass connection (B) to a pyrex condenser (C). At the ground glass joint (D) a pyrex tube (E) lead to the U-Tube (F), which had a seal of NaOH solution. (G) was a similar U-Tube used as an indicator for complete absorption of OsO_4 vapors in (F). See sketch.

6 N HCl was added in excess of the theoretical amount. The necessary quantity of alcohol was added in small amounts as the reaction progressed.

The contents of the flask were warmed gently at first. Too vigorous heating caused the molten OsO_4 to blacken and too great a quantity of OsO_4 escaped to the NaOH U-tube. The solution took on a brownish color which became darker and darker. Oily droplets of OsO_4 refluxed from the walls of the flask for a time and finally ceased to appear. At this point the temperature was raised to incipient boiling until the liquid in the flask became red and transparent. The reaction was then complete. The time consumed was about three hours.

This solution was stable, had no odor of OsO_4, and could be evaporated on the steam-bath to a viscous syrup from which long reddish needles separated on cooling. These had a similar appearance to H_2PtCl_6 crystals and were probably the corresponding H_2OsCl_6.

(c) Precipitation of $(NH_4)_2OsCl_6$

The crystals of H_2OsCl_6, moistened with HCl, dissolved in water to a clear golden yellow solution. There were usually present, however, some flakes of black OsO_2, so that the diluted solution had to be filtered. Saturated NH_4Cl solution precipitated brick red $(NH_4)_2OsCl_6$. The chloroosmate was filtered on a Hirsch funnel using a hardened filter and washed with saturated NH_4Cl until the washings became colorless.

It was found that the salt could be safely dried in a drying oven even at 110°C.

The mother liquors from the NH_4Cl precipitation together with the washings were evaporated to dryness on the steam-bath without loss of osmium, pulverized in a mortar and reduced in hydrogen. A large porcelain crucible, covered with a quartz plate provided with a hole through which hydrogen passed, facilitated the recovery of the osmium. A flame was directed downward on the quartz plate, in order to sublime any NH_4Cl which condensed.

The recovered osmium was black, due to adsorbed hydrogen.

(d) Reduction of $(NH_4)_2OsCl_6$ to Metal

Reduction of the chloroosmate to metal was carried out in a combustion tube, in an atmosphere of hydrogen, heated finally to dull redness of the heating coils of the electric furnace.

Pure dry nitrogen, from which oxygen had been removed, displaced the hydrogen while the temperature was at the maximum. The osmium sponge was cooled in an atmosphere of nitrogen and had a bluish gray color. Metal prepared in this way emitted no odor of OsO_4 when standing in contact with air for several months in a loosely stoppered bottle.

Without the use of nitrogen the metal was black and contained considerable adsorbed hydrogen. Even after the boat and metal had cooled to room temperature, this osmium would catch fire in coming in contact with air as the combustion tube was opened.

7. Spectroscopic Evidence of Purity

148.9 g of $(NH_4)_2OsCl_6$ were prepared. Samples of this material, converted to metal, were investigated by the Spectroscopic Section of the Bureau of Standards for lines due to traces of impurities.

The osmium sponge was burned in fresh electrodes of pure copper. Their spectrogram No. 1279 showed that the samples were identical and that there was no trace of Fe, Pt, Pd, Ir, Ru, Rh, or Ca.

8. Advantages of This Method of Preparation

(1) The handling of the extremely poisonous OsO_4 can be carriedout with no danger to the operator.

(2) The reagents employed in the reduction of OsO_4 to H_2OsCl_6 are volatile ones which allow of easy purification.

(3) The purification cycle can be conveniently repeated.

(4) The recovery of osmium from filtrates is readily accomplished.

(5) Osmium of the highest purity can be made in appreciable amounts.

THE ATOMIC WEIGHT OF OSMIUM

1. Introduction

This work was undertaken with the idea of determining the ratio, Os : OsO_4. This ratio, although not a good one mathematically, is ideal in that it is a direct one, involving only the arbitrary standard, oxygen, and the element whose atomic weight it is desired to determine.

Partly because of the great difficulties involved in carrying out this determination and partly because $(NH_4)_2OsCl_6$ and $(NH_4)_2OsBr_6$ could be prepared in a high state of purity, attention was concentrated upon the analysis of these two compounds. The method of preparation of the $(NH_4)_2OsCl_6$ differed from those used by other workers and the $(NH_4)_2OsBr_6$ introduced a new ratio.

2. Historical

The atomic weight of osmium has been determined by Berzelius, by Fremy, indirectly by Deville and Debray, by Seubert and by Seybold.

This work may be conveniently divided into two classes:

(1) Approximate Determination

The earliest attempt was that of Berzelius[1] who analyzed

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[1] Ann. der Phys. (Pogg) 13, 530 (1828)

Note -- See also Bibliography of the Metals of the Platinum Group, Bulletin 694, U.S.Geological Survey, by J. L. Howe and H. C. Holtz. National Academy of Sciences, Vol. 16, Third Memoir, The Constants of Nature, Part V, A Recalculation of the Atomic Weights, 4th Ed., by F. W. Clarke.

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potassium chlorosmate, K_2OsCl_6. He dried the salt at beginning redness in a current of chlorine and reduced it in hydrogen. 1.3165 g of this salt lost 0.3805 g of chlorine, the residue consisting of 0.401 g of KCl and 0.535 of osmium. Calculating only from the ratio between the Os and the KCl, the data give Os = 198.94.

Fremy[2] synthesized osmium tetroxide. He employed a

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[2] Compt. Rend., 19, 468 (1844)
Journ. Prakt. Chem., 33, 410 (1844)

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scheme analogous to that used by Dumas and Stas[3] to determine

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[3] Ann. Chim. Phys. (3) 1, 1

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the atomic weight of carbon. Fremy burned osmium in oxygen, in which case the osmium was converted quantitatively into osmium tetroxide, and absorbed the latter by means of fragments of caustic potash.

He carried out the combustion in a tube divided into two parts by a constriction. He placed the metal in the first part of the tube and the fragments of caustic potash in the other part. A potash tube, serving as an indicator for complete absorption, was attached to the above apparatus. This tube did not change weight showing that the OsO_4 was quantitatively absorbed by the first potash tube. He avoided the use of corks, although he does not say how, which immediately reduces the OsO_4. Fremy states only the final result Os = 199.65, although he makes the statement that it is the result of many analyses of which he gives the details in his memoir. In conclusion,he states that although his experiences are in accord with those of Berzelius, he does not consider the atomic weight of osmium as definitely fixed, and that he will return to that question in a particular memoir.

A reference in the literature to R. Schneider[1] in connection with the atomic weight of osmium shows that he merely made a recalculation and not a determination.

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[1] Ann. der Phys. 88, 314 (1853)

Deville and Debray[1] made a vapor density determination

[1] C. R., 44, 1101 (1857)
Encyclopedie Chemique, 30, (1) 73
30, (3) 122
Ann. des Mines 5° Serie, t XVI, p. 83 (1859)

of OsO_4 by the Dumas Method. They found that one liter of OsO_4 vapor at standard conditions weighed 11.475 g.

From their data the atomic weight can be calculated. The atomic weight turns out to be 193.84.

(2) Exact Determination

When the periodic law came into general acceptance, it became clearly evident that the values of Berzelius and of Fremy for the atomic weight of osmium must be several units too high.

The first work of real importance was that carried out by Seubert[2] who prepared and analyzed two salts, namely,

[2] Berichte, 21, 1839 (1888)

$(NH_4)_2OsCl_6$ and K_2OsCl_6, thus following the method of Berzelius. Seubert was the first to give any details of procedure.

Seubert obtained osmium from two sources. The first was that from an osmiridium sample, known to be very pure, contained in a museum. This osmiridium was pulverized by fusion

with zinc and subsequently ignited with $BaCl_2$ in a current of moist chlorine. A sublimate of "osmium chloride" was obtained which dissolved in alcohol with a red color. NH_4Cl precipitated a fiery red "osmium salmiak". This precipitate served for the preparation of $(NH_4)_2OsCl_6$ I. The NH_4Cl excess was removed with ice-cooled water, the remaining salt dissolved in water at 50°C and the solution filtered. Heating for a long period or to a higher temperature was avoided because of the decomposition of the $(NH_4)_2OsCl_6$ under these conditions. The deep golden solution was evaporated over H_2SO_4 at reduced pressure.

A second crop of crystals was obtained from the mother liquor of $(NH_4)_2OsCl_6$ I which served as a starting point for the preparation of K_2OsCl_6. The resulting metal was fused with KCl in a current of dry chlorine. The K_2OsCl_6 thus obtained was washed free of excess KCl and dissolved in luke warm water. This solution was evaporated to crystallization.

The second source was 10 g "reinsten osmiums" given Seubert by Dr. Th. Schuchardt in Görlitz. Schuchardt prepared the osmium by his own process, the nature of which he did not divulge, but his name stood as guarantee of its purity.

This metal served for the preparations II. It was taken up with KCl and chlorine gas to form K_2OsCl_6 and only

the first crystallization used for analyses (K_2OsCl_6 II). The later crystallizations as well as the mother liquor furnished the material for $(NH_4)_2OsCl_6$ II.

The K_2OsCl_6 was reduced in hydrogen, the KCl washed out and the metal taken up in NaCl and chlorine to form Na_2OsCl_6. The concentrated solution of Na_2OsCl_6, filtered free of unattacked metal, gave a precipitate of $(NH_4)_2OsCl_6$ upon addition of saturated NH_4Cl. The adsorbed NaCl was drained out by dilute NH_4Cl and finally by ice-cooled water. Recrystallizations (does not say how many) furnished material for analyses $(NH_4)_2OsCl_6$ II .

The salts were pulverized in an agate mortar and dried for many weeks over P_2O_5 under diminished pressure.

In the analysis the $(NH_4)_2OsCl_6$ was reduced in hydrogen, and after cooling the H_2 was removed with CO_2. The boat with the metal was placed in a glass stoppered tared vessel for weighing. The total chlorine in the compound was caught and precipitated as AgCl.

Series	$(NH_4)_2OsCl_6$	Os	6 AgCl
I	(1.8403 g	0.7986	3.5897
	(2.0764	0.9029	4.0460
	(2.1501	0.9344	4.1950
II	2.1345	0.9275	4.1614

Hence, we have for the percentage of osmium and for the chlorosmate proportional to 100 parts of AgCl

Series	Per cent Os	AgCl : Salt
I	(43.446	51.266
	(43.484	51.320
	(43.458	51.254
II	43.453	51.293
		51.283 ± 0.0099

The K_2OsCl_6 was reduced in the same manner. The volatile portion, 4 HCl, was determined by precipitation as AgCl. The 2 KCl was washed out of the osmium and weighed.

Series	K_2OsCl_6	Os	2 KCl	4 AgCl
I	2.5148		0.7796	2.9837
II	2.1138	0.8405	0.6547	2.5076

Hence, with salt proportional to 100 parts of AgCl in the last column, we have

Series	Per cent Os	Per cent KCl	Ag : Salt
I		31.000	84.091
II	39.762	30.973	84.102
			Mean = 84.097 ± 0.0030

In a later paper Seubert[1] reported two more reductions of $(NH_4)_2OsCl_6$.

[1] Liebig's Annalen, 261, 358 (1891)

Series	Salt	Os	Per cent Os
III	(2.6687	1.1597	43.456
	(2.6937	1.1706	43.457

These determinations with the four in his first paper give a mean percentage of Os in $(NH_4)_2OsCl_6$ of 43.459 ± 0.0036.

The $(NH_4)_2OsCl_6$ in the second paper was prepared by means of Na_2OsCl_6. The concentrated Na_2OsCl_6 solution was filtered, diluted with water and an equal volume of 50 per cent alcohol added. To this solution was added in slight excess NH_4Cl in 50 per cent alcohol.

The salt was collected on a suction filter and washed with dilute alcohol. Recrystallization from water gave the salt for analysis. The salt was dried over P_2O_5 at reduced pressure. It was pulverized in an agate mortar before being analyzed.

Seubert in his second paper prepared specimens of K_2OsCl_6.

I. The osmium was taken up in KCl and chlorine and the K_2OsCl_6 quickly recrystallized.

II. K_2OsCl_6 was prepared as in Series II of his former paper.

III. A solution of Na_2OsCl_6 was made, alcohol added, K_2OsCl_6 precipitated by KCl and this salt quickly recrystallized.

Seubert determined the percentage osmium in K_2OsCl_6 by reducing the salt in H_2 to a mixture of 2 KCl + Os, and then volatilizing the KCl in a current of hydrogen, using a platinum tube 40 cm long and 1.9 cm in diameter. The reduction

took place in a glass tube. The boat was then transferred to the platinum tube. The volatilization of the KCl took from 35 to 40 minutes.

With the exception of the determination of Os in K_2OsCl_6 the procedure was the same as in his earlier paper.

Series	No.	K_2OsCl_6 grams	Os grams	Per cent Os
I	1	1.1863	0.4691	39.543
	2	0.9279	0.3667	39.519
	3	1.0946	0.4330	39.558
	4	1.6055	0.6451	39.558
II	1	0.4495	0.1778	39.555
	2	0.8646	0.3417	39.531
III	1	0.7044	0.2781	39.593
	2	1.2742	0.5041	39.562
	3	1.0466	0.4141	39.566
				39.553 ± 0.0052

Series	No.	K_2OsCl_6 grams	2 KCl grams	Per cent KCl
I	1	2.2032	0.6820	30.955
	2	2.0394	0.6312	30.950
	3	2.7596	0.8544	30.961
III	1	2.4934	0.7710	30.922
	2	2.8606	0.8843	30.913
	3	1.8668	0.5768	30.898
	4	1.2227	0.3778	30.899
			Mean	30.931
			Earlier Set	31.000
				30.973
		Mean of all nine determinations		30.941 ± 0.0079

The single percentage of osmium in Seubert's first paper is negligible.

The last work done upon the atomic weight of osmium was carried out by Seybold[1] who analyzed $(NH_4)_2OsCl_6$. He followed

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1 Inaugural Dissertation 1912, Frederich-Alexanders University, Erlangen.

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the procedure of Subert.

Seybold obtained "pure" osmium from the firm of W. C. Heraeus. It was converted to Na_2OsCl_6. Seybold varied Seubert's method of preparing $(NH_4)_2OsCl_6$ in that he added the hydrochloric acid solution of Na_2OsCl_6 to an alcoholic solution of NH_4Cl. The precipitated $(NH_4)_2OsCl_6$ was recrystallized from hydrochloric acid. This salt, $(NH_4)_2OsCl_6$ I, was red and finely crystalline.

For $(NH_4)_2OsCl_6$ II the hydrochloric acid solution of Na_2OsCl_6 and the alcoholic NH_4Cl were filtered together into a large beaker. The formation of $(NH_4)_2OsCl_6$ was then not so rapid. These crystals were dark brown. The salt was recrystallized, washed with alcoholic water, then with absolute alcohol and centrifuged. After two weeks drying over P_2O_5 no trace of OsO_4 was noticeable.

For Series III the procedure was the same as for II except that the solutions were filtered separately. The crystals were not dark brown but bright red. They were washed and centrifuged as in II. After standing for a month over P_2O_5 they were odorless.

Previous to making the analyses, Seybold pulverized the salt in an agate mortar and dried it at 105°C for eleven to fourteen periods of about 3-1/2 hours each.

The apparatus was first drained of air by means of CO_2, and then of CO_2 by H_2. The boat containing the salt which had been placed in the glass combustion tube was heated by means of a small burner and finally by the full flame of a shallow fan tail burner. Too rapid heating caused small amounts of osmium to be entrained with the volatile NH_4Cl. When the reduction was complete the boat was heated to redness for some time while a brisk current of hydrogen passed and then it was cooled in CO_2. The boats were placed in glass stoppered vessels and weighed after three hours.

In Series I and III the osmium possessed a blue gray color. In Series II it was black and less dense. After a short time it smelled strongly of OsO_4 while that in I and III possessed but a faint odor.

The results of Seybold's analyses are as follows:

Series	No.	$(NH_4)_2OsCl_6$ grams	Os grams	Per cent Os
I	1	0.92831	0.40110	43.209
III	1	1.37982	0.59639	43.215
	2	0.86661	0.37448	43.212
	3	1.17170	0.50642	43.221
	4	1.31312	0.56730	43.203
			Mean	43.212
II	1	4.94681	2.14915	43.447
	2	3.78304	1.64378	43.452
	3	1.44792	0.62958	43.413
				43.437

According to Seybold Series II were weighed openly in the air. Series III were weighed in glass stoppered vessels. One is left to infer that Series I were weighed in the same manner as III.

Seybold is not clear in regard to the manner in which he displaced the hydrogen by CO_2 after the completion of the reduction.

In his general description of the reduction he stated that the boat was heated to redness in a current of hydrogen and cooled in CO_2. In describing Series III he stated that the boat was cooled in hydrogen, the hydrogen then being displaced with CO_2.

We will then consider this point later.

Seybold considered that Series I and III have a greater claim to accuracy and reported the atomic weight to be 189.4. He rejected Series II on the ground that the $(NH_4)_2OsCl_6$ might have some enclosed mother liquor. However, he ruled out this possibility because the salt on long standing did not continue to emit the odor of OsO_4. He concluded that the high results were due to the absorption of oxygen by the metallic osmium.

F. W. Clarke[1] states that the analyses of $(NH_4)_2OsCl_6$

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1 Memoirs of the National Academy of Sciences, Vol. XVI, Third Memoir, The Constants of Nature, Part V, A Recalculation of the Atomic Weights, 4th Ed., 1920.

by Seybold are of slight importance because they are not concordant. He says it would be justifiable to reject Seybold's work arbitrarily, but is perhaps better to give it some weight and to regard the two groups as one, with a mean percentage of 43.296 ± 0.0257. This value, combined with that of Seubert, 43.459 ± 0.0036, gives a general mean of

$(NH_4)_2OsCl_6 : Os = 100 : 43.452 \pm 0.0035.$

Clarke says that Seybold's determinations practically reject themselves.

The ratios for osmium are now as follows:

(1) Per cent Os in $(NH_4)_2OsCl_6$, 43.452 ± 0.0035

(2) 6 AgCl : $(NH_4)_2OsCl_6$ :: 100 : 51.283 ± 0.0099

(3) 4 AgCl : K_2OsCl_6 :: 100 : 84.097 ± 0.0030

(4) Per cent Os in K_2OsCl_6, 39.553 ± 0.0052

(5) Per cent KCl in K_2OsCl_6, 30.941 ± 0.0079

To reduce these values we have

Ag = 107.880 ± 0.00016

Cl = 35.4605 ± 0.00011

N = 14.0081 ± 0.00008

K = 39.0975 ± 0.00011

H = 1.0078 ± 0.00001

Hence,

From ratio

4	Os =	190.386 ± 0.0399
5		190.979 ± 0.0933
3		191.122 ± 0.0173
1		191.212 ± 0.0194
2		192.314 ± 0.0852
General Mean	Os =	191.073 ± 0.0117

The international value appearing in atomic weight tables is Os = 190.9.

3. Criticism of Previous Work on the Atomic Weight

We will consider only the work of Fremy, Seubert and of Seybold.

Regarding the synthesis of OsO_4, Fremy gives only the barest details. His value is too high for the atomic weight. The ratio Os : OsO_4 is an ideal one although mathematically it is not very good. A determination of this ratio has many disadvantages, namely:

(a) The absorption of OsO_4 by caustic alkali is not stric tly analogous to the absorption of CO_2. OsO_4 possesses but feeble acid properties and is extremely susceptible of reduction to lower oxides. The alkaline osmate solutions are not strictly stable for OsO_4 is lost when an alkaline solution of OsO_4 is warmed.

(b) If one chose to condense and freeze OsO_4 very low temperatures would have to be used, because OsO_4 has a considerable vapor pressure. The apparatus for combusting the metal and condensing the tetroxide without loss would necessarily be complicated. It should be borne in mind that organic lubricants on stopcocks cause reduction of OsO_4 and deposition of osmium. Even a ground glass surface becomes blackened when exposed to the tetroxide vapors.

(c) The determination of the density of OsO_4, necessary for reduction to vacuo weight, is by no means easy to carry out.

Seubert's work is open to some criticism.

(a) Seubert's osmium for Series II was taken "on fath" to be of highest purity. For Series I, he used "very pure" osmiridium with zinc and subsequently ignited with $BaCl_2$ in moist chlorine, giving a sublimate of "osmium chloride". No tests were made of purity in either case.

(b) In his $(NH_4)_2OsCl_6$ II, he used NaCl and chlorine to effect the solution of the osmium. From a concentrated solution of the resulting Na_2OsCl_6, he precipitated $(NH_4)_2OsCl_6$ by saturated NH_4Cl. Although he washed the $(NH_4)_2OsCl_6$ with dilute NH_4Cl and ice cooled water and recrystallized from water, some NaCl might have remained.

(c) Water hydrolyses and decomposes $(NH_4)_2OsCl_6$. OsO_4

being evolved can be detected very easily by its characteristic odor. At the same time there is a blackening of the salt. Even ice cooled water causes the evolution of OsO_4.

(d) The ratios depending upon chloride determination are subject to the errors involved in absorption, precipitation, filtration and drying.

(e) The determination of KCl depends upon the skill of the investigator to wash it free from the osmium sponge.

(f) In the analysis of $(NH_4)_2OsCl_6$, reduction was made in hydrogen. After cooling, the hydrogen was displaced by CO_2. Osmium sponge resulting from such a reduction adsorbs H_2 strongly and it is very doubtful whether CO_2 in the cold will completely displace all adsorbed hydrogen. Any H_2 adsorbed reacts with the oxygen of the air and the OsO_4 odor can be detected. Osmium sponge reduced in hydrogen and cooled in hydrogen is black and will catch fire when exposed to the air. Osmium sponge free from H_2 is bluish gray and is stable in the air.

(g) No description of the method of heating the reduction tube is given. This is an important point, because too sudden heating, such as is liable in the case of using a Bunsen burner, is not unlikely to cause loss of osmium by entrainment with the NH_4Cl.

(h) Simple drying over P_2O_5 may not be sufficient to completely dehydrate the salts. No mention of the formation

of H_2O on reduction of the salt is made. If the salt contains oxygen, H_2O will appear on reduction.
However, Seubert's work stands as the best we have on the atomic weight of osmium.

The last atomic weight research done on osmium, that of Seybold, does not seem to be of any value. It is open to all the objections mentioned under Seubert's work, where the salt $(NH_4)_2OsCl_6$ is concerned, with the exception that Seybold did not attempt to recrystallize from water.

Having seen fit to find objections in the foregoing work, the author attempts to meet those objections as follows:

(a) Metallic osmium of highest possible purity, whose spectrogram showed the absence of Fe, Pt, Pd, Rh, Ir, Ru, and Ca, was first prepared to be used as a starting point for the preparation of the salts for analysis.

(b) $(NH_4)_2OsCl_6$ was prepared for analysis by a method wholly different in part from any used to date. All reagents concerned were volatile ones which allowed of easy purification. Thus the resulting sponge would be free of nonvolatile salts.

(c) It was found by actual experience that $(NH_4)_2OsCl_6$ undergoes decomposition when recrystallized from water. From hydrochloric acid solution, the salt can be recrystallized and no odor of OsO_4 was detected at any time during the recrystallizations.

(d) The author chose such a ratio that absorptions, precipitations, and filtrations were avoided.

(e) The potassium salts were not prepared for analysis.

(f) Pure dry nitrogen was used instead of CO_2 to displace H_2 after reduction. The use of N_2 avoided any possibility of products of reduction which would be injurious to the osmium. Furthermore, the N_2 was lead in at the final temperature of reduction in order that the best conditions obtained for the complete displacement of adsorbed hydrogen.

(g) An electric tube furnace was used to heat the reduction tube. The temperature was capable of careful control. Thus the mechanical loss of osmium by too sudden heating was avoided.

(h) The value of the ratio Os : $(NH_4)_2OsCl_6$ depends upon the accuracy of obtaining the salt absolutely dry and in its normal composition as well as realizing the osmium to be completely reduced and uncontaminated by anything, even hydrogen. It was found that P_2O_5 did not effect complete drying. Heating the salt to 170°C in dry nitrogen caused further loss in weight and the salt was able to resist decomposition. Precaution was made to observe the appearance of any H_2O vapor on reduction of the salt.

(i) The method of preparation of the salt $(NH_4)_2OsCl_6$ for analysis was equally applicable for the preparation of

$(NH_4)_2OsBr_6$ for analysis. This salt has never been previously prepared for atomic weight analysis. This salt and the corresponding potassium salt give five more ratios on which to base the atomic weight of osmium.

(1) Per cent Os in $(NH_4)_2OsBr_6$

(2) 6 AgBr : $(NH_4)_2OsBr_6$

(3) 4 AgBr : K_2OsBr_6

(4) Per cent Os in K_2OsBr_6

(5) Per cent KCl in K_2OsBr_6

4. Preparation of Reagents

Hydrochloric Acid

C.P. hydrochloric acid of commerce was diluted to 30 per cent HCl with distilled water of the laboratory.

This acid was distilled twice from a ground glass stoppered Pyrex flask whose side arm extended to a considerable distance into the tube of a condenser. In each case the first and last portions were rejected. The middle fraction from the second distillation was caught and stored in a ground glass stoppered Jena bottle.

Ammonium Chloride Solution

A concentrated solution of NH_4OH was prepared at the Bureau of Standards by distilling NH_3 from a tank into pure distilled water of the laboratory.

The ammonium chloride solution was prepared by neutralizing the twice distilled HCl with NH_3 gas gently driven over from the above NH_4OH solution.

The NH_4Cl solution was made and stored in a Jena bottle having a ground glass stopper.

Water

The distilled water of the laboratory was distilled once from alkaline permanganate solution in a Pyrex distilling flask whose side arm, drawn out, fitted snugly into the block tin tube of the condenser. The middle fraction of this water was distilled from a dilute H_2SO_4 solution. The middle fraction of the second distillation was caught and stored in a ground glass stoppered Jena bottle.

The water was distilled a short time previous to use.

Alcohol

Two liters of ethy alcohol (95 per cent) were distilled using a Vigreux column. The first and last portions were rejected. The middle fraction was allowed to stand over CaO for several days and then distilled without the use of the column. This middle fraction was again distilled without CaO or the column and the resulting middle fraction saved.

Hydrobromic Acid

Chemically pure hydrobromic acid of commerce was distilled twice from a solution of recrystallized C. P. calcium bromide of commerce. The first and last fractions were rejected in each case.

A third distillation was made from a solution of recrystallized potassium bromide of commerce. The middle fraction was used in the preparation of H_2OsBr_6.

Ammonium Bromide

A portion of the above hydrobromic acid was neutralized by gently distilling NH_3 into the acid in the manner described for the preparation of ammonium chloride.

5. The Preparations of the Compounds for Analysis

$(NH_4)_2OsCl_6$

138.9 g of $(NH_4)_2OsCl_6$ was prepared from osmium obtained from Baker and Company, in the manner described under the preparation of pure osmium. Spectroscopic examination of the metal resulting from the reduction of the $(NH_4)_2OsCl_6$ showed it to be of the same purity as that prepared from the Russian residues.

A portion of the 138.9 g of $(NH_4)_2OsCl_6$ was converted to metal which in turn was burned to OsO_4. H_2OsCl_6 was formed. The solution was evaporated to a syrup, diluted with water containing HCl, filtered, and $(NH_4)_2OsCl_6$ precipitated by NH_4Cl. The purified HCl and NH_4Cl were used here.

This last salt was recrystallized from 2 N HCl (purified acid) by making a saturated solution at 85°C, filtering through a Gooch crucible holding ahardened filter using suction, and rapidly cooling the filtrate with an ice bath. The solution was stirred while cooling.

The recrystallized $(NH_4)_2OsCl_6$ having the characteristic reddish brick color, was filtered off on a Gooch crucible, using a hardened filter. It was then centrifuged, washing with successive portions of absolute alcohol.

The salt was dried over P_2O_5 at reduced pressure for five days. It was then dried at 130°C in a drying oven for several hours, after which the salt was pulverized in an agate mortar. This preparation was known as Baker and Company $(NH_4)_2OsCl_6$ I.

$(NH_4)_2OsBr_6$

The metal obtained from preliminary analyses of $(NH_4)_2OsCl_6$ was used to prepare $(NH_4)_2OsBr_6$.

The $(NH_4)_2OsCl_6$ used in the preliminary analyses was prepared in the manner described above, from a portion of the 148.9 g of $(NH_4)_2OsCl_6$ mentioned under the spectroscopic evidence of purity in the first part of this paper.

The metal was converted to OsO_4 and thence to H_2OsBr_6, the addition of alcohol being unnecessary. The evaporated solution, acid with HBr, was diluted, filtered and $(NH_4)_2OsBr_6$ precipitated.

(a) A portion of this salt was recrystallized from 20 per cent hydrobromic acid in the manner described under the preparation of $(NH_4)_2OsCl_6$ I.

The recrystallized salt was black with a tinge of brown. Successive portions of absolute alcohol were used to wash the crystals.

The salt was dried over P_2O_5 at reduced pressure and also in a drying oven at 130°C for several hours.

The salt was pulverized in an agate mortar.

The preparation was known as Russian $(NH_4)_2OsBr_6$ II.

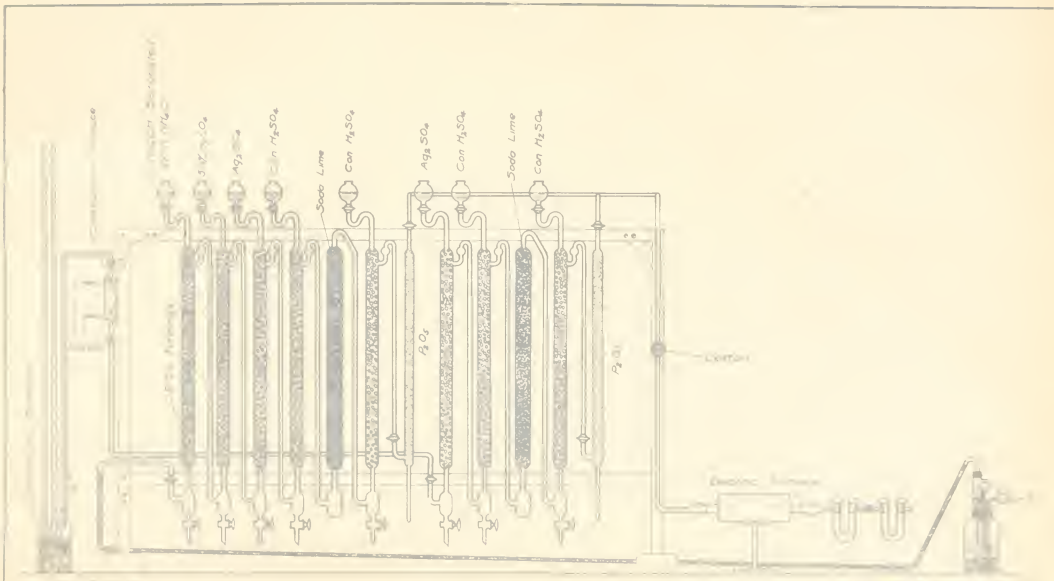
(b) A second preparation of $(NH_4)_2OsBr_6$ was made by recrystallization from a saturated solution which had been filtered through a Blue Ribbon filter. In this case, however, the salt was not washed with alcohol but with a (dilute) solution of hydrobromic acid. It was dried in a desiccator over P_2O_5 for five days, pulverized in an agate mortar and dried at 130°C in a drying oven for 18 hours. This preparation was known as Russian $(NH_4)_2OsBr_6$ III.

6. Balance and Weights

The balance used for the analyses of Baker and Company $(NH_4)_2OsCl_6$ I and Russian $(NH_4)_2OsBr_6$ II was an Ainsworth QA. It was kept in a room maintained at practically constant temperature.

The balance used for the analyses of Russian $(NH_4)_2OsBr_6$ III was a Rüprecht Kg balance, B.S. 4911, provided with an outer case of blackened copper.

The weights used were obtained from Christian Becker, Inc., New York, N.Y. They were known as Class S Analytical Weights. 100 grams to 1 gram were lacquered brass; 500 milligrams to



APPARATUS FOR THE ANALYSIS OF THE OSMIUM SALTS.

PHOTOGRAPHIC LABORATORY
BUREAU OF STANDARDS
WASHINGTON, D. C.
2931 4
NEGATIVE NO.

50 milligrams were platinum; 20 milligrams to 1 milligram were aluminum.

The weights were calibrated by Mr. A. T. Pienkowsky of the Bureau of Standards.

The weighings were done by the method of substitution and swings.

7. Apparatus Used for the Analysis

The apparatus, which is shown in the accompanying sketch, consisted, in the main of the following parts.

(a) Apparatus for the purification and drying of nitrogen.

(b) Apparatus for the generation, purification, and drying of hydrogen.

(c) The tube wherein the reduction of the salt took place.

Commercial nitrogen, from the fractionation of liquid air was bubbled into a bottle containing 1 : 1 NH_4OH saturated with NH_4Cl in contact with C. P. copper turnings.[1] The gas

[1] W. L. Badger, Jour. Ind. Eng. Chem. 12, 161 (1920)

then passed through a tube about 7-1/2 feet in length containing the same reagent. The tube was bent such that at either end the gas stream came in contact with copper turning extending above the solution.

The scrubbing and drying towers[2] were mounted on an iron

[2] E. Wichers -- Dissertation, University of Illinois 1917.

frame. For the nitrogen there were seven towers, each 50 cm in height. The first contained copper turnings with 1 : 1 NH_4OH saturated with NH_4Cl. The second contained 50 per cent H_2SO_4. The third was filled with acidified Ag_2SO_4 solution. The fourth held conc. H_2SO_4. The fifth was a solid tower containing soda-lime. The sixth had conc. H_2SO_4 and the seventh tower contained P_2O_5 which had been distilled into the tube.

Hydrogen was generated in a cell containing dilute KOH solution. The electrodes were of platinum foil. Hydrostatic pressure forced the hydrogen through the system. An electrically heated porcelain tube containing palladium asbestos and palladium quartz was placed between the cell and the scrubbing towers. A temperature of about 500°C was maintained in the tube.

There were five scrubbing and drying towers for the hydrogen. The first tower contained Ag_2SO_4 solution, acidified with H_2SO_4. The second contained conc. H_2SO_4. The third held soda-lime. The fourth was filled with conc. H_2SO_4 and the last tower contained distilled P_2O_5.

The reduction tube was made of a good grade of German combustion glass.

Heating was done by the Hoskins electric furnace, Type 70.

Two U-tubes containing glass beads and conc. H_2SO_4 sealed the exit of the reduction tube.

For the construction of the electrolytic cell and the scrubbing train the author wishes to express his thanks to Mr. E.O. Sperling of the Bureau of Standards.

8. Reduction of the Osmium Salts to Metal

In the analysis of Baker and Company $(NH_4)_2OsCl_6$ I and Russian $(NH_4)_2OsBr_6$ II, the pulverized salt was further dried by placing the boat containing the salt in the reduction tube. A current of dry nitrogen passed for 3-1/2 hours while the temperature was maintained at about 170°C. In $(NH_4)_2OsCl_6$ I, Exp. 5, the salt was dried for 6-1/2 hours at 170°C.

The boats used were of Royal Meissen porcelain which had been brought to constant weight.

Tared thin glass tubes provided with ground glass stoppers were always used to hold the boats during the process of weighing.

In the decomposition of the salt $(NH_4)_2OsCl_6$ I and $(NH_4)_2OsBr_6$ II by hydrogen, the reduction tube was swept with a current of nitrogen for 1 hour, then with a current of hydrogen for 1 hour before the heating unit was turned on. The tube was warmed very gradually, requiring two hours toreach a final temperature of somber redness of the nichrome heating coils.

Nitrogen then displaced hydrogen at this temperature for 1 hour. The current was shut off, and the upper half of the

furnace was raised. After 1/2 hour the furnace was removed to allow the reduction tube to cool to room temperature, nitrogen continuing to pass until the boat was removed.

In the analysis of some preliminary samples, especially those prepared by mere recrystallization from water, showed a trace of moisture when the salt began to reduce in hydrogen.

The osmium sponge resulting from the reductions was bluish grey in color, emitted no odor of OsO_4 during the period of weighing, nor after two months standing in a loosely stoppered bottle.

In the analysis of $(NH_4)_2OsBr_6$ III the reduction tube was swept with nitrogen for 4 hours and with hydrogen for 3 hours before the heating unit was turned on. No formation of moisture was observed during the reduction of the salt to metal. In Exp. 2, the osmium was heated in hydrogen for double the length of time of that in Exp. 1.

Results of Analysis

Baker and Company $(NH_4)_2OsCl_6$ Series I

Exp.	Weight of $(NH_4)_2OsCl_6$ in vacuo grams	Weight of osmium in vacuo grams	Per cent Os	Atomic Weight
1	1.46116	0.63688	43.587	
2	2.80587	1.22226	43.560	
3	2.32007	1.01021	43.542	
4	1.93756	0.84390	43.555	
5	2.92857	1.27597	43.569	
			43.563	192.074
	$(NH_4)_2OsCl_6$: Os = 100 : 43.563			
	Os = 192.074			

Russian $(NH_4)_2OsBr_6$ Series II

Exp.	Weight of $(NH_4)_2OsBr_6$ in vacuo grams	Weight of osmium in vacuo grams	Per cent Os	Atomic Weight
1	4.17909	1.13522	27.164	

Russian $(NH_4)_2OsBr_6$ Series III

Exp.	Salt in vacuo grams	Metal in vacuo grams	Per cent Os
1	1.72778	0.46909	27.150
2	0.98661	0.26783	27.146

Average of $(NH_4)_2OsBr_6$ II and III = 27.153

$(NH_4)_2OsBr_6$: Os = 100 : 27.153

Os = 192.172

Average of all eight experiments = 192.111.

Summary

1. A convenient method was developed for the preparation of considerable quantities of spectroscopically pure osmium.

2. The reaction between OsO_4 and dilute HCl, and the analogous reaction using HBr, furnish H_2OsCl_6 and H_2OsBr_6 which can be used as a starting point to prepare a greater variety of osmium salts for atomic weight analysis.

3. Osmium sponge, from which adsorbed hydrogen has been displaced in the hot by nitrogen is not attacked rapidly by the air.

4. The results of the analyses made give for the atomic weight of osmium the value 192.111.

Vita

The author received his early education in the public schools of Great Falls, Montana. He attended the University of Montana, at Missoula, from 1911 to 1915, receiving the degree of Bachelor of Arts in Chemistry from that institution in 1915. From September 1915 to December 1917, he was a Graduate Assistant in the Department of Chemistry, Cornell University. During the same years he pursued work toward the Doctorate, which was interrupted by the World War.

From January 1919 to date he has been associated with the Platinum Metals Section of the Bureau of Standards, Washington, D. C.

From February 1921 to February 1922, the author attended the Johns Hopkins University.